V. *Observations on the Electro-chemical Influence of long-continued Electric Currents of Low Tension. By* GOLDING BIRD, *F.L.S., F.G.S., Lecturer on Experimental Philosophy at Guy's Hospital, &c. Communicated by* THOMAS BELL, *Esq., F.R.S.*

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1. SCARCELY any branch of scientific investigation has yielded more important and interesting results than electro-chemistry, which, as is well known, in the hands of a DAVY, demonstrated the existence of the alkaline metals, and formed a memorable and important epoch in the history of chemical science. Sir HUMPHRY DAVY availed himself of the energetic influence of voltaic currents in a high state of tension, and elicited by means of large batteries. To M. BECQUEREL, however, we are almost entirely indebted for our knowledge of the chemical agency of feeble currents in reducing certain refractory oxides to the metallic state, although it must not be forgotten that Dr. EDMUND DAVY applied the power of weak currents of electricity to the detection of the metallic poisons, by reducing them to the reguline state. BUCHOLZ appears, in 1807, to have succeeded in obtaining crystals of metallic copper by the aid of a simple voltaic circle. But it is to our illustrious countryman Dr. FARADAY that we owe our acquaintance with the interesting circumstance of the power possessed by a current of very low intensity (elicited by a single pair of platinum and zinc plates) in decomposing several saline combinations, as the iodide of potassium, sulphate of soda, &c., and isolating their respective constituents. In offering the following observations, I have not sufficient presumption to suppose them to be possessed of any very important or original value; but being, as they are, the results of carefully repeated experiments, and containing an account of what I believe to be some previously unobserved facts, I deem myself justified in submitting them to the notice of the Royal Society.

2. The facts recently pointed out by M. BECQUEREL of the energetic power exerted by weak electric currents in effecting the reduction not only of the oxides of copper, lead, or tin, but even of glucina, alumina, and silica, are probably very well known to every one. This philosopher obtained these interesting results by means of a single pair of plates, placing the solution of the metallic salt in a glass tube closed at one end by means of a plug of moistened clay, and immersed in a weak solution of common salt: on placing then a compound metallic arc formed of zinc and platinum in the solutions in such a manner that the platinum leg might be immersed in the tube containing the metallic solution, (to which M. BECQUEREL applies the general term of "negative tube,") whilst the zinc dips in the solution of salt, decomposition ensues, and after a lapse of time, varying from a few hours to some weeks, the metal is gene-

rally deposited from its solution on the platinum plate in a more or less crystalline form. M. Becquerel did not attribute the reduction of the metal to the electric current alone, but conceived that three distinct causes, at least, concurred in producing this effect. The decomposition of the water and of the common salt by the electric current set in motion, and the transference of hydrogen and soda through the clay diaphragm to the negative tube, where the alkali unites with the acid holding the metal in solution, causing the deposition of its oxide, which, while in its nascent state, is reduced by the hydrogen, and precipitated in its metallic form on the negative electrode; thus regarding the hydrogen furnished by the decomposition of the water as the actual reducing agent. In some cases, a fourth cause is supposed to be superadded to these, as when a body is used for the negative electrode, for which the metal in solution has a certain degree of affinity; a well-known example of which is found in the reduction of potassium from a solution of potassa when submitted to comparatively weak voltaic action in contact with mercury. Mercury is not the only metal applicable to this purpose, M. Becquerel having frequently used iron with success. He states that the solutions of the pure chlorides of zirconium, glucium, titanium, silicon, &c., refused to yield to the reducing action of weak electric currents, until after the addition of a small quantity of chloride of iron: this the current readily decomposed, precipitating the iron in a crystalline form on the platinum plate, (negative electrode,) which deposit speedily *induces* the commencement of the decomposition of the more refractory salts. This circumstance he attributes to the affinity of the iron for the other metal tending to the formation of an alloy, and expressly states, that when *perfectly pure* the above-mentioned chlorides *did not undergo the slightest decomposition*. I have ascertained, however, that if the electric current is *continuous*, notwithstanding its weak tension, this reduction and decomposition may be effected without the presence of iron, or indeed of any other metal in solution, excepting that which we are attempting to reduce. I must apologize for the above rapid sketch of some of M. Becquerel's researches, the introduction of which into this paper appeared to be necessary for the better understanding the results of my own more limited investigations.

3. On commencing my experiments on the chemical power of electric currents of weak tension, I soon found the want of an apparatus capable of affording an *equal* and *continuous* current of low intensity, which appeared to me to be absolutely necessary for the success of my experiments. In the common electromotor the currents are at first very energetic, but soon cease, or become so feeble as to be scarcely able to traverse a fluid medium unless fresh portions of the exciting fluid is added from time to time. Even Professor Daniell's very ingenious single-pair battery, although most excellent for electro-magnetic purposes, and affording considerable quantities of electricity, yet required the occasional addition of fresh acid and sulphate of copper, which was inconvenient when required to be kept in constant action for some weeks, besides occasioning an irregularity in the intensity of the current. The *quan-*

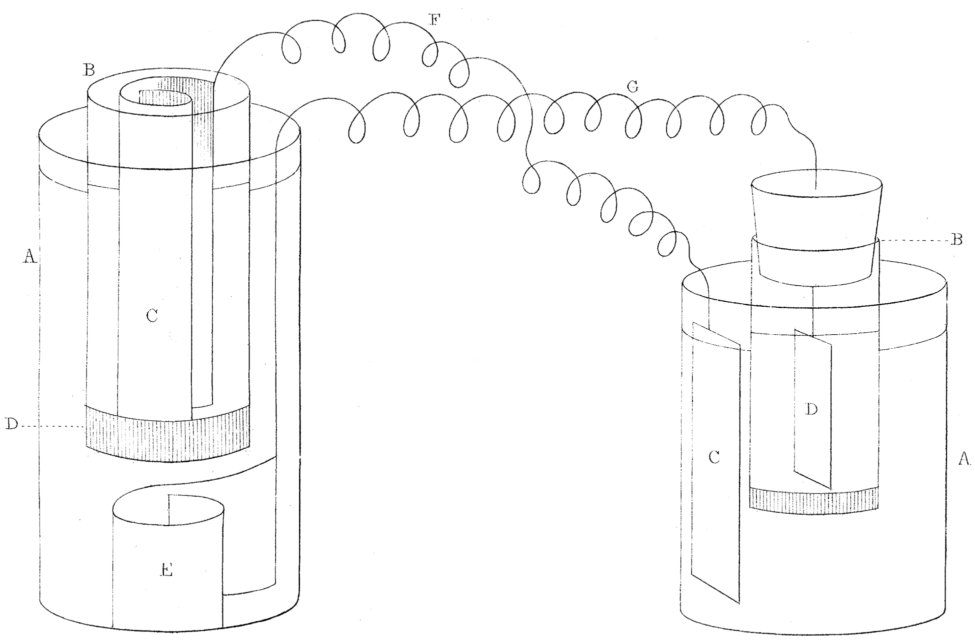

Fig. 1. *Fig. 2.*

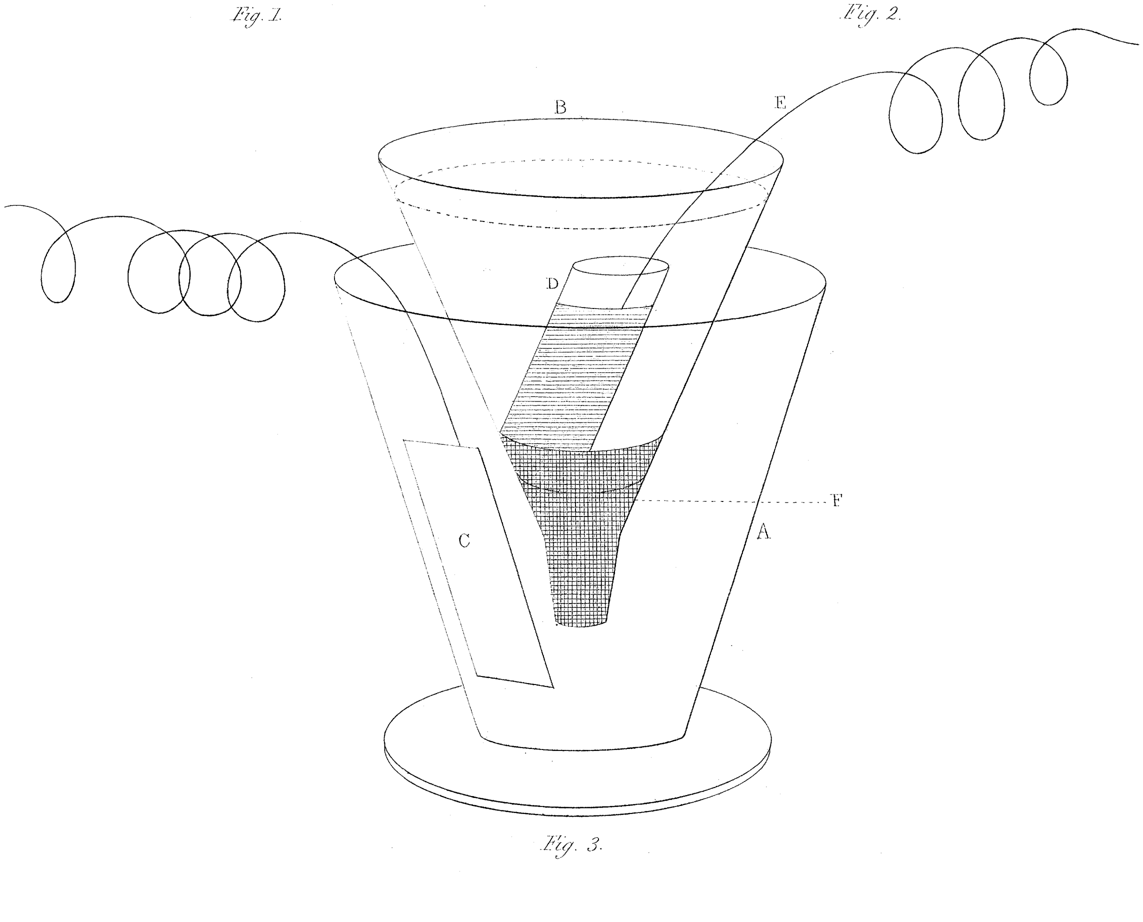

Fig. 3.

Fig. 1. The battery connected with the decomposing apparatus.

2. The decomposing apparatus.

3. A modification of Fig. 2. for obtaining the amalgams of the alcaline metals.

NB. The dotted line in Fig. 3. shews the level of fluid in the funnel above the mercury.

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tity of electricity appearing to be by no means so important as a *continuous and equable current.* For similar reasons Mr. MULLINS's modification of Professor DANIELL's battery was found equally objectionable; added to which the currents evolved are liable to be materially affected by the admixture of the exciting fluids through the membranous partition, which always takes place sooner or later by endosmosmic action.

4. After several experiments I was induced to prefer the following apparatus, (which after all is but a slight modification of Professor DANIELL's,) in consequence of its affording a constant and regular current of electricity of very weak tension, continuing for several weeks or even longer without any fresh addition of exciting fluid. A glass cylinder, 1·5 inch in diameter and 4 inches in length, was closed at one end by means of a plug of plaster of Paris 0·7 inch in thickness: this cylinder was fixed by means of corks inside a cylindrical glass vessel about 8 inches deep and 2 inches in diameter. A piece of sheet copper, 6 inches long and 3 inches wide, (having a copper conducting wire soldered to it,) was loosely coiled up, and placed in the small cylinder with the plaster bottom: a piece of sheet zinc of equal size was also loosely coiled up, and placed in the larger external cylinder (being furnished like the copper plate with a conducting wire). The larger cylindrical glass being then nearly filled with weak brine, and the smaller with a saturated solution of sulphate of copper, the two fluids being prevented from mixing by the plaster of Paris diaphragm, the apparatus is complete*; and if care is taken that the fluids in the two cylinders are at the same level, will continue to afford a continuous current of electricity for some weeks, the sulphate of copper being very slowly decomposed. So feeble is the current evolved by an apparatus of this kind, that on connecting the two conducting wires with a common galvanometer, (having but one needle suspended on a pivot,) a deviation to only 10° or 12° took place: with NOBILI's galvanometer, with nearly astatic needles, a deviation to 90° immediately ensued, as might be expected from the greater delicacy of the instrument. So small, indeed, is the quantity of electricity evolved by the apparatus I have described, as compared to that evolved by the ordinary electromotor, that I was unable to produce the simplest form of electro-magnetic rotation by its aid. After it has been in action for some weeks, chloride of zinc is found in the external cylinder, and beautiful crystals of metallic copper, frequently mixed with the ruby protoxide (closely resembling the native ruby copper ore) and large crystals of sulphate of soda, are found adhering to the copper plate in the smaller cylinder, especially on that part where it touches the plaster diaphragm.

* So simple an apparatus scarcely requires an illustration: in the accompanying outline sketch I have, however, figured it, to prevent any error arising from the account in the next not being sufficiently explicit.

Fig 1. represents the battery connected with the apparatus described in paragraph 4.

A. The external cylinder.

B. The smaller one; with D. The plaster of Paris bottom.

C. The coil of copper in the cylinder B, having the conducting wire F soldered to it.

E. The coil of zinc with the wire G soldered to it.

5. If the two copper conducting wires belonging to the little apparatus just described are immersed in water acidulated with sulphuric acid, action soon commences, bubbles of hydrogen appearing at the wire connected with the zinc plate, whilst that connected with the copper plate became tarnished, oxydized, and at last partly dissolved, giving a blueish tint to the fluid; affording an approach to the decomposition of water by a single pair of plates. For the success of this experiment, it is, as might be expected, necessary that the *positive* electrode at least should be formed of a readily oxidizable metal; for when both wires were of platinum, no evidence of decomposing action ensued.

6. If, instead of acidulated water, the wires were immersed into a solution of nitrate or acetate of lead, no *immediate* action ensued, but in about fifteen minutes, or even less, some elegant and delicate feathers of metallic lead, which rapidly increased in size, appeared at the negative electrode. This effect did not occur when *both* conducting wires were of platinum; but when the *negative* electrode only was composed of that metal, the reduction of the lead continued with apparently increased energy. From these experiments, as well as many others of a similar kind which it is unnecessary to detail, it appears fair to presume, that in availing ourselves of the *reducing* agency of feeble currents, or at least of those elicited by a single pair of plates, it is necessary that the positive electrode should be composed of a readily oxidizable metal: thus using a kind of battery of *two* cells, in which the wires forming the electrodes, and the fluid submitted to experiment, form the contents of the second cell.

7. But few metallic solutions yield so readily as those of lead to the reducing agency of weak currents; and where a longer time and continuance of action is required to effect the reduction, the decomposing apparatus of M. Becquerel will be found a useful addition to the little battery (4.), with the substitution of a plug of plaster of Paris for one of clay. This piece of apparatus is, in fact, a counterpart of the battery itself, consisting, like it, of two glass cylinders, one within the other, the smaller one having a bottom or floor of plaster of Paris fixed into it: this smaller tube may be about half an inch wide and three inches in length, and is intended to hold the metallic solution submitted to experiment, the external tube in which it is immersed being filled with a weak solution of common salt *. Into the latter solution a slip of amalgamated zinc, (for the positive electrode,) soldered to the wire coming from the copper plate of the battery (4.), is immersed, whilst for the negative electrode a slip of platina foil, fixed to the wire from the zinc plate of the battery, passes through a

* Fig. 2. in the sketch represents this apparatus connected with the battery.

A. The larger tube.

B. The smaller one, with the plaster bottom.

C. The electrode of amalgamated zinc connected by the wire F with the copper plate C of the battery (Fig. 1.).

D. The negative electrode of platinum connected by the wire G with the zinc plate of the battery (Fig. 1.).

cork fixed in the mouth of the smaller tube, and dips into the metallic solution it contains.

8. When a solution of the chlorides or nitrates of iron, copper, tin, zinc, bismuth, antimony, lead, or silver, is placed in the smaller tube of the apparatus (7.), and connexion made with the battery * in the manner already described, action is almost instantly apparent, water is decomposed, and torrents of minute bubbles of hydrogen are evolved at the surface of the platinum plate, (negative electrode,) which continues for a short time, sometimes, indeed, lasting for hours; a circumstance depending apparently upon the degree of facility with which the metal under experiment is reduced. Thus with solutions of copper, scarcely a bubble appears, the metal being almost immediately reduced, all the hydrogen being probably employed from the instant of completing the circle, for that purpose: with solutions of lead, tin, or silver, the evolution of hydrogen continues for a short time only, and ceases as soon as the minutest portion of reduced metal appears on the platinum plate; but with solutions of iron and manganese the evolution of gas frequently continues for six, eight, or ten hours, or even longer; the evolution of hydrogen thus seeming to bear something like an inverse ratio to the ease with which metal is reduced. After the hydrogen has ceased to appear at the negative electrode, striæ of the reduced metal, which rapidly increase, are deposited on the surface of the platinum.

9. The metals thus reduced generally, but not invariably possess a perfectly metallic lustre, are always more or less crystalline, and often very beautifully so, affording a considerable contrast to the irregular soft spongy masses obtained from the same solutions by means of large batteries. The crystals of copper obtained by the process just detailed (8.), rival in hardness and malleability the finest specimens of native copper, which they much resemble in appearance. The crystallization of bismuth, lead, and silver by these means, is very beautiful, that of the former metal being lamellar, of a lustre approaching to that of iron, but with the reddish tint peculiar to this metal. Silver may be thus obtained of a snowy and indeed dazzling whiteness, usually under the form of needles.

10. The metallic solutions hitherto mentioned as yielding to the action of the little battery are, as is well known, equally acted on by larger voltaic batteries, consisting of a considerable number of alternations, the metal being reduced in a spongy form, often destitute of a metallic appearance. But there are some metals which are deposited from their solutions as oxides only, when acted on by currents from large batteries, and yet are deposited in a brilliant metallic form if submitted to the action of the currents from the little apparatus already described (4). Of these nickel is an example: a solution of its chloride or sulphate, when placed in the smaller tube of the decomposing apparatus (7.), yielding after some hours a crust of metallic nickel on the negative electrode, often of a silvery lustre on the surface immediately

* It may here be proper to remark, that by the word battery in the course of the following observations I always allude to the modification of Prof. Daniell's battery described in § 4.

applied to the platinum, that portion of the crust more in contact with the fluid being generally black, and frequently covered with a layer of the hydrated and gelatinous green oxide.

11. Finding that by means of this apparatus I could command a weak but continuous current capable of reducing even the more refractory metallic oxides, I was anxious to ascertain whether the current was sufficiently energetic to cause the reduction of those oxides which (as silica) do not yield to powerful batteries, and which M. Becquerel obtained only alloyed with iron.

12. The solution of silicon used by M. Becquerel was prepared by dissolving gelatinous silicic acid in hydrochloric acid of commerce, which always contains iron; this on being submitted to the action of a single pair of plates deposited an alloy of iron and silicon on the negative electrode. As this solution contains but a very small quantity of silicon, I substituted a solution of fluoride of silicon in alcohol obtained by passing a current of the gaseous fluoride into strong alcohol. On filling the smaller tube of the decomposing apparatus (7.) with this solution, and making the connexion with the battery in the manner already described, bubbles of hydrogen were copiously evolved at the surface of the platinum plate (negative electrode), which continued for eight or ten hours, when the platinum appeared to be tarnished, and in twenty-four hours a copious deposit of silicon had taken place on the platinum, to the surface of which it firmly adhered. Around the reduced silicon, and suspended in the fluid, was a dense gelatinous cloud of silicic acid. On quickly withdrawing the slip of platinum, dipping it in water, and then pressing it between folds of bibulous paper it was dried, and freed from any adhering solution. The silicon was nearly black and granular, under a lens, exhibiting a tendency to a crystalline form. It was not deposited on the platinum in a confused or irregular manner, but in longitudinal striæ, which appeared to follow the direction of certain lines of minute eminences on the surface of the piece of platinum, produced apparently by scouring it with fine sand and a piece of cork before being used for the construction of the negative electrode.

13. The silicon thus procured becomes of a snowy whiteness when ignited in the flame of a spirit lamp, and falls off the platinum in thin flakes, being in fact converted into silicic acid. It is not very easy to oxidate the whole, in consequence of the flakes of the acid forming an incrustation over the subjacent silicon, and protecting it from the oxidating influence of the air even at a red heat. A portion of the silicon *removed* from the platinum did not appear to dissolve in hydrochloric acid; but when the platinum itself with the firmly adhering silicon was immersed in the acid, slow action ensued, bubbles of hydrogen being evolved from the *exposed surface of platinum*, the silicon very slowly disappearing; the solution being probably occasioned by the formation of a simple voltaic circle, the silicon and platinum being the metals, and the acid the exciting fluid. When an aqueous solution of hydrofluosilicic acid is substituted for the fluoride of silicon, the metalloid is reduced, but slower and in

smaller quantity; differences arising in all probability from the smaller quantity of silicon present in the solution.

14. I have frequently had occasion to observe that when an aqueous solution of hydrofluosilicic acid has been submitted to the action of currents of low tension (from the battery already described (4.)) continued during two or three weeks, a considerable deposition of gelatinous silicic acid takes place around the reduced silicon; mixed with which, or precipitated in a zone on the sides of the tube, especially if of small diameter, or even upon the platinum electrode itself, frequently appear minute crystalline grains of sufficient hardness to scratch glass, and appearing translucent under the microscope. These minute crystals I have no hesitation in stating to be crystallized silicic acid, closely resembling its natural form of *quartzose sand.*

15. I next attempted to form potassium with the same apparatus, but failed, as I had anticipated, from the presence of water, which indeed would react on the potassium as soon as reduced. I therefore endeavoured to form its amalgam, well knowing that when dissolved in mercury a very weak electric current is sufficient to prevent the oxidating influence of water upon it; and by using a modification of the decomposing apparatus before described (7.) I succeeded perfectly. In place of the smaller tube containing the metallic solution, I used a small glass funnel*, the beak of which was carefully filled up with plaster of Paris: on this plaster floor I placed a piece of glass tube closed at one end, about 0·5 inch in length and 0·2 inch in diameter, and half filled with pure mercury; this tube was not placed vertically, but inclined so as to form an angle of about 40° with the plaster floor of the funnel, which with its contents was partly immersed in the weak brine contained in the larger cylinder of the decomposing apparatus. The external cylinder communicated as before with the copper plate of the battery, by means of a slip of amalgamated zinc dipping into the brine it contained. The funnel was then nearly filled with a solution of chloride of potassium, and a piece of platinum wire connected with the zinc plate of the battery being twisted into a flat spiral at one end so as to present a larger surface, was immersed in the mercury contained in the little tube submerged in the saline contents of the funnel. The circuit being thus completed, galvanic action soon became apparent, bubbles of hydrogen being evolved from the surface of the mercury (which now formed the negative electrode) in a very curious manner, not in confused and rapid streams, but in large and distinct bubbles, which very slowly appeared, and performed several gyratory movements on the surface of the fluid metal before they were evolved. Not unfrequently a single bubble only was seen, which continued

* This variety of the apparatus is shown in fig. 3. of the outline sketch.

A. The external vessel containing the salt and water.

B. The funnel containing the alkaline salt required, with its plaster floor F.

C. The positive electrode of amalgamated zinc communicating with the copper plate of the battery (fig. 1.).

D. The little tube containing mercury immersed in the alkaline solution with a platinum wire E, connected with the zinc plate of the battery (fig. 1.) dipping into it.

playing on the surface of the mercury for half an hour, or even longer, before it rose to the surface of the fluid. In about eight or ten hours the mercury had swollen to double its former bulk, and part of it had actually crept* up the platinum wire to the height of 0·3 inch above the level of the other portion, adhering to the wire like so much tenacious mucilage. On dipping a piece of turmeric paper into the contents of the funnel it turned brown, demonstrating the presence of an alkali. The mercury was removed from the little tube as quickly as possible, and poured into distilled water, which acted upon it, causing the evolution of hydrogen gas from its whole surface, and became alkaline from the formation and solution of the oxide of potassium or potass. The film of mercury adhering to the platinum wire remained on it for some days, giving it the appearance of having been amalgamated. This experiment, several times repeated, yielded precisely similar results, from which I think that I am justified in stating that potassa can be reduced by means of the feeble current elicited by a single pair, or as the positive electrode was formed of an oxidizable metal, in the opinion of some, perhaps of two pairs of plates.

16. By submitting in the same apparatus a solution of chloride of sodium to the influence of the battery, analogous results were obtained. An amalgam of sodium being formed, although a much longer time was required, and the result of the experiment, although quite decided, was by no means so distinct as in the case of the reduction of potassium.

17. But of all the saline solutions that I have yet submitted to experiment, none afforded such conclusive and interesting results as those of ammonia. The ammonium being reduced with almost as much ease as copper or tin, when a solution of its chloride (hydrochlorate of ammonia) is submitted to the action of the voltaic current in contact with mercury, in the same manner as chloride of potassium or sodium. The same adhesion and creeping up of the mercury along the wire (15.) is observed, and after a few hours the fluid metal swells to five or six times its former bulk. On removing it quickly and drying it, by allowing it to fall on bibulous paper the amalgam of ammonium is obtained of a buttery consistence, possessing a dull silvery colour, and yielding a peculiar crackling, or (if I may be allowed the expression) an emphysematous sensation to the finger on pressing it: on being immersed in water it very slowly gave off hydrogen, and yielded a solution of ammonia.

18. By far the most satisfactory method of obtaining this amalgam is by using for the negative electrode a piece of platinum wire coiled up at one end, after it has been amalgamated by dipping it into the ammoniacal amalgam obtained by the last described process (17.). A minute quantity of mercury is thus made to adhere to the wire, which being connected with the zinc side of the battery, is dipped into a solution of hydrochlorate of ammonia contained in the smaller tube of the apparatus used in effecting the reduction of silicon (7.). The circuit being completed, a few bubbles

* This peculiar creeping up of the mercury along the wire does not take place if the little tube holding the fluid metal is placed in a vertical position.

of hydrogen are disengaged from the amalgamated wire, which soon cease, and in an hour or two, a leaden grey spongy mass is observed adhering to the wire, which is sometimes sufficiently bulky to fill the tube, and putting on much of the external appearance of a mass of cellular galena. This mass consists of a spongy amalgam of ammonium, containing a very minute proportion of mercury; it is lighter than the solution in which it is immersed, for on adroitly separating a portion of it, it rises to the surface and rapidly decomposes water, hydrogen being evolved and ammonia formed.

19. It is a very curious and interesting fact, that although this spongy ammoniacal amalgam cannot be kept immersed in water even for a few instants without the formation of ammonia, yet as long as it is connected with the negative electrode of the battery, it may be preserved without change for days and weeks. The instant the connexion with the battery is broken, a mass of this amalgam, as large as a walnut, appears to vanish in a few seconds, torrents of minute bubbles being given off, and a scarcely appreciable quantity of mercury being left on the wire. On again closing the connexion with the battery decomposition recommences, and the amalgam is reproduced.

20. From a review of the results of these experiments, we cannot help being struck with the very energetic power of electric currents of weak tension; currents of sufficient energy to reduce to the metallic state oxides on which currents of higher tension from large batteries are comparatively powerless. This fact, although pointed out by Becquerel and other philosophers, has (as far as I am aware) never been before shown to hold good in the reduction of the alkaline metals. Potassium and ammonium not having, I believe, been previously obtained by the weak current emanating from the chemical action of saline solutions on a single pair of plates; and silicon, although obtained by Becquerel combined with iron, has not been procured before in a pure state by electric currents, at least by those of feeble tension*.

In conclusion I may be permitted to observe, that in applying weak electric currents to the reduction of metallic oxides, it is *absolutely necessary that a continuous current be employed, and that its cessation even for an instant is often fatal to the success of the experiment on hand,* which cessation or suspension, as far as my experiments have gone, the modification I have proposed of Professor Daniell's battery appears to be capable of obviating.

Guy's Hospital,
January 20, 1837.

* Some other curious circumstances connected with the decomposing electro-chemical power of currents of low tension have fallen under my observation, but have not yet been sufficiently examined to authorize their publication as facts. Some of these I may perhaps at a future period, with the permission of the Society, have the honour of submitting to its notice.